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UPPER AND LOWER BOUNDS FOR GROUND STATE

SECOND ORDER PERTURBATION ENERGY

by

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and

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Addenda and Errata to WIS-TCI-28 - "Upper and Lower Bounds for Ground

State Second Order

Perturbation Energy"

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Abstract Five lines from bottom should read:

" ··· wave function, the Hylleraas principle is presented ··· " .

p. 3   Third line from the top: change "is" to "are" .

Fourth line from the top: should read " ··· arbitrary

additive constant."

Three lines above Eq. (6): change "Sections" to "sections" .

p. 6   One line below Eq. (17): delete "only slightly" .

Below Eq.(18) insert: "Here $\S$ $\underset{\sim}{G}$ may be arbitrarily large."

p. 8   Replace last two lines with: "the true function F . The

right hand side of (27) is independent of a . For any

other property depending on the magnitude of $\bar{F}$, the most

probable value of the constant a is" .

p. 12,13 Replacement is on opposite side of this page.

p. 14   Ref. 8. Add at end in place of J. O. Hirschfelder reference:

"A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. A233, 70 (1956);

A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. A238, 269 (1956)."

p. 15   Ref. 13. Last equation should read:

" ··· $= \int r_{12}^{-1} K(r_2)^{-1} \left[\cdots \right.$ " .

UPPER AND LOWER BOUNDS FOR GROUND STATE

SECOND ORDER PERTURBATION ENERGY*

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ABSTRACT

The first-order perturbation equation, using the Dalgarno-Lewis
formulation, is arranged in a form analagous to the Poisson equation
for the electrostatic potential produced by a charge distribution in
a medium of variable dielectric constant. Thus, the Thomson and
Dirichlet variational principles of electrostatics can be used to
obtain approximate solutions to the first-order perturbation equation
for systems in either the ground state or the lowest energy state of a
given symmetry. The Thomson principle provides a useful lower bound
to the second-order perturbation energy. The Dirichlet principle is
derivable from the Rayleigh-Ritz or Hylleraas principles and gives an
upper bound to the second-order energy. For excited states, the
Sinanoglu principle provides the upper bound. By optimizing the scaling
of the trial perturbed wave function, both the Hylleraas and the
Sinanoglu principles are presented in a somewhat improved form. As an
example, the polarizability of atomic hydrogen is used to illustrate
both the Thomson and Dirichlet principles and to place upper and lower
bounds on the polarizability.

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I. Introduction

The first order perturbation equation in molecular quantum mechanics can be expressed in a form which is similar to the equation for the electrostatic potential of a charge distribution in a medium of variable dielectric constant. The second-order perturbation energy is proportional to the electrostatic energy of this charge distribution. By this analogy, the well-known Dirichlet and Thomson variational principles of electrostatics[1,2] can be used to provide upper and lower bounds for the second-order perturbation energy of a molecule in its ground state. The Dirichlet principle for the upper bound is derivable from the quantum mechanical Rayleigh-Ritz principle and is somewhat better than the Hylleraas principle[3,4] which is frequently used for perturbation problems. The Thomson principle for the lower bound is far better than the Weinstein-MacDonald principle[4,5,6] which previously provided our best lower bound estimate (without explicit consideration of the energy of the first excited state). The calculation of the polarizability of atomic hydrogen is used as a simple example to show the efficacy of the Thomson and the Dirichlet principles. Following Sinanoglu[7], the Dirichlet principle can be extended to give upper bounds for the energy of molecules in excited states by making use of the unperturbed wave functions for each of the lower energy states. The Thomson principle

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might be extended to give lower bounds to the energy for excited states. However, when the perturbation equation is separable, the solutions may be obtained by quadrature and there is little need for a variational principle.

The Dalgarno-Lewis procedure[8,9] for determining explicit solutions to the perturbation equations has made it feasible to apply perturbation theory to a wide class of molecular problems where complete sets of solutions are not known for the unperturbed system[10]. Perturbation treatments have the advantage over variational methods that they permit the system itself to select the proper type of terms which should be included in the trial wave function. From a knowledge of the trial wave function through the first order, the energy can be calculated accurately through the third order. For many chemical purposes this is sufficient accuracy.

Dalgarno and Lewis[8,9] express the first-order perturbed wave function as a product of a function F and ψ_o. Here ψ_o is the zeroeth order (or unperturbed) wave function[11] for the state under consideration (which is designated by the subscript "o"). For convenience we take ψ_o to be real. If V is the perturbation potential, the first-order perturbation equation can be expressed in the form

$$\nabla \cdot (\psi_o^2 \nabla F) = 2\psi_o(V - \epsilon_o^{(1)})\psi_o \tag{1}$$

Here $\epsilon_o^{(1)}$ is the first order perturbation energy,

$$\epsilon_o^{(1)} = \int \psi_o V \psi_o \, d\underset{\sim}{r} \tag{2}$$

The second and third-order energies, $\epsilon_o^{(2)}$ and $\epsilon_o^{(3)}$, are

$$\epsilon_o^{(2)} = \int \psi_o(V - \epsilon_o^{(1)})\psi_o F \, d\underset{\sim}{r} \tag{3}$$

$$\epsilon_o^{(3)} = \int F \psi_o(V - \epsilon_o^{(1)})\psi_o F \, d\underset{\sim}{r} \tag{4}$$

The product $F \psi_o$ must satisfy the same boundary conditions and the

same conditions of continuity, square integrability, and continuity of the first derivatives (except at interior points where the potential energy is singular) as is normally expected of stationary state wave functions. Equation (1) defines F except for an arbitrary constant. Usually this constant is adjusted so as to make $\int \psi_0 \, F \, \psi_0 \, d\underset{\sim}{r} = 0$. If ψ_s is the unperturbed wave function for the state "s" and the unperturbed energies are ϵ_s and ϵ_0 for the two states,

$$\int \psi_s \, F \, \psi_0 \, d\underset{\sim}{r} = (\epsilon_0 - \epsilon_s)^{-1} \int \psi_s \, V \, \psi_0 \, d\underset{\sim}{r} \qquad (5)$$

If Eq. (1) is separable, F can be determined by quadrature if the state under consideration is either the ground state or the lowest energy state of a given symmetry. For other states, difficulties are encountered since F may have poles at points where ψ_0 has nodes. For excited states, there are special procedures for determining F provided that Eq. (1) is separable[12]. Except in Section VI, we shall confine our attention to the ground state or the lowest energy state of a given symmetry. The higher order perturbation equations can be written in the same general form as Eq. (1). Therefore, without difficulty, the results of the following Sections can be generalized to the higher orders of perturbation.

The first order perturbation relation, Eq. (1), may be regarded as a Poisson equation

$$\nabla \cdot (K \nabla \phi) = -4\pi \rho \qquad (6)$$

for the electrostatic potential $\phi = F$ produced by the charge distribution $\rho = -(2\pi)^{-1} \psi_0 (V - \epsilon_0^{(1)}) \psi_0$ in a medium of variable dielectric constant $K = \psi_0^2$. Furthermore, the electrostatic self-energy of the charge distribution is $U = \frac{1}{2} \int \rho \phi \, d\underset{\sim}{r} = -(4\pi)^{-1} \epsilon_0^{(2)}$. Thus, the Thomson and Dirichlet principles of electrostatics can be applied to obtain lower and upper bounds for $\epsilon_0^{(2)}$ provided that singularities in F arising from nodes in ψ_0 are avoided by restricting the discussion to the ground state or to the lowest energy state of a given symmetry.

II. <u>Thomson and Dirichlet Principles in Electrostatics</u>[1,2]

In a medium of variable dielectric constant K , the self-energy U of a charge distribution ρ may be written in a number of different ways:[13]

$$U = \tfrac{1}{2}\int \rho\phi \, d\underset{\sim}{r} = (8\pi)^{-1}\int K \, \nabla\phi\cdot\nabla\phi \, d\underset{\sim}{r} = (8\pi)^{-1}\int K \, \underset{\sim}{E}\cdot\underset{\sim}{E} \, d\underset{\sim}{r} \qquad (7)$$

Here the electric field $\underset{\sim}{E}$ is minus the gradient of the electrostatic potential,

$$\underset{\sim}{E} = -\nabla\phi \qquad (8)$$

If in place of the true potential ϕ (which satisfies Eq. (6)) and the true electric field $\underset{\sim}{E}$ (which satisfies Eq. (8)) we use the trial potential $\bar{\phi}$ and the trial field $\underset{\sim}{\bar{E}}$, the three integrals in Eq. (7) are no longer equal nor equal to U . However, we have the following inequalities:

<u>Thomson's Principle</u> states that the self-energy given in terms of the trial electric field constitutes an upper bound on U ,

$$U \le (8\pi)^{-1}\int K \, \underset{\sim}{\bar{E}}\cdot\underset{\sim}{\bar{E}} \, d\underset{\sim}{r} \qquad (9)$$

subject to the condition that the trial electric field satisfies the Poisson equation in the form

$$\nabla\cdot K \, \underset{\sim}{\bar{E}} = 4\pi\rho \qquad (10)$$

The equality in (9) only applies if $\underset{\sim}{\bar{E}}$ also satisfies Eq. (8) in which case the trial field is equal to the true field.

<u>Dirichlet's Principle</u> provides a lower bound to the self-energy. It states that

$$U \ge 2\pi\left[\int \rho\bar{\phi} \, d\underset{\sim}{r}\right]^2 \Big/ \int K \, \nabla\bar{\phi}\cdot\nabla\bar{\phi} \, d\underset{\sim}{r} \qquad (11)$$

for any trial potential $\bar{\phi}$ that goes to zero at infinity. The equality in (11) is only obtained when $\bar{\phi}$ satisfies Eq. (6) and is therefore equal to the true potential.

Equations of the Poisson type occur in connection with a wide variety of physical phenomena. Thus, the Thomson and Dirichlet principles have been used to determine the magnetic permeability in multiphase systems[14], the effective diffusion constant in poly-electrolyte solutions[15], the Fermi-Thomas energy of atomic systems[16], and the evaluation of quantum mechanical exchange and coulombic integrals[2]. In addition, the Dirichlet principle has been used to determine the Brownian movement in many-particle systems[17] and the diffusion and viscous flow in concentrated suspensions[18]. With such a history of successful applications, it is not surprising that the Thomson and Dirichlet principles can be usefully applied to perturbation problems.

III. Lower Bound for $\epsilon_o^{(2)}$, Thomson's Principle

Thomson's principle can be applied to perturbation theory provided that neither $\psi_o(V- \epsilon_o^{(2)})\psi_o$ nor F have singularities. The first condition is satisfied if the Rayleigh-Schrodinger perturbation theory is applicable (without special considerations). The second condition is satisfied if the state "o" under consideration is the lowest energy state of a given symmetry. Under these conditions, by analogy with Eqs. (9) and (10),

$$\epsilon_o^{(2)} \geq -\tfrac{1}{2} \int \psi_o^2 \; \bar{G} \cdot \bar{G} \; d\underset{\sim}{r} \tag{12}$$

subject to the condition that the trial "field" $\bar{G}$ satisfies the Poisson equation in the form

$$\nabla \cdot (\psi_o^2 \bar{G}) = -2\psi_o(V- \epsilon_o^{(1)})\psi_o \tag{13}$$

The equality in (12) applies if, and only if, $\bar{G} = -\nabla F$.
PROOF:

First, let us prove that the equality in (12) applies for the

true "field" $\underset{\sim}{G} = -\nabla F$. Multiplying Eq. (1) by F and integrating over all space,

$$\tfrac{1}{2} \int F \, \nabla \cdot (\psi_o^2 \, \nabla F) d\underset{\sim}{r} = \int \psi_o (V - \epsilon_o^{(1)}) \psi_o \, F \, d\underset{\sim}{r} = \epsilon_o^{(2)} \qquad (14)$$

The conditions for the applicability of Thomson's principle, stated above, insure that Gauss' theorem can be applied to the left-hand-side of Eq. (14)

$$\tfrac{1}{2} \int_{\substack{\text{all space}}} F \, \nabla \cdot (\psi_o^2 \, \nabla F) d\underset{\sim}{r} = \tfrac{1}{2} \int_{\substack{\text{boundary surface} \\ \text{at infinity}}} \psi_o^2 \, F \, \nabla F \cdot d\underset{\sim}{S} - \tfrac{1}{2} \int_{\substack{\text{all space}}} \psi_o^2 \, \nabla F \cdot \nabla F \, d\underset{\sim}{r} \qquad (15)$$

The surface integral in Eq. (15) vanishes because of the boundary conditions imposed upon the stationary state wave function ψ_o and its perturbation $F \psi_o$ (they go to zero faster than any negative power of the distance as the distance approaches infinity). Combining Eqs. (14) and (15) and using the definition of $\underset{\sim}{G}$,

$$\epsilon_o^{(2)} = -\tfrac{1}{2} \int \psi_o^2 \, \underset{\sim}{G} \cdot \underset{\sim}{G} \, d\underset{\sim}{r} \qquad (16)$$

Furthermore, Eq. (1) can be written in terms of $\underset{\sim}{G}$,

$$\nabla \cdot (\psi_o^2 \, \underset{\sim}{G}) = -2\psi_o (V - \epsilon_o^{(1)}) \psi_o \qquad (17)$$

Now let us consider a trial field $\underset{\sim}{\bar{G}}$ which differs only slightly from the true field,

$$\underset{\sim}{G} = \underset{\sim}{\bar{G}} + \delta \underset{\sim}{G} \qquad (18)$$

Substituting Eq. (18) into Eq. (16),

$$\epsilon_o^{(2)} = -\tfrac{1}{2} \int \psi_o^2 \, \underset{\sim}{\bar{G}} \cdot \underset{\sim}{\bar{G}} \, d\underset{\sim}{r} - \int \psi_o^2 \, \underset{\sim}{\bar{G}} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r} - \tfrac{1}{2} \int \psi_o^2 \, \delta \underset{\sim}{G} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r}$$

$$\qquad (19)$$

$$= -\tfrac{1}{2} \int \psi_o^2 \, \underset{\sim}{\bar{G}} \cdot \underset{\sim}{\bar{G}} \, d\underset{\sim}{r} - \int \psi_o^2 \, \underset{\sim}{G} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r} + \tfrac{1}{2} \int \psi_o^2 \, \delta \underset{\sim}{G} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r}$$

Substituting Eq. (18) into Eq. (17) and imposing the condition (17),

$$\nabla \cdot (\psi_0^{\,2} \delta \underset{\sim}{G}) = 0 \tag{20}$$

Multiply Eq. (20) by F and integrate over all space, to give

$$\int F \, \nabla \cdot (\psi_0^{\,2} \delta \underset{\sim}{G}) d\underset{\sim}{r} = 0 \tag{21}$$

If $\delta \underset{\sim}{G}$ has no singularities, Gauss'theorem may be applied to Eq. (21) to give

$$\int \psi_0^{\,2} \, \delta \underset{\sim}{G} \cdot \nabla F \, d\underset{\sim}{r} = 0 \tag{22}$$

Making use of Eq. (22) and the definition $\underset{\sim}{G} = -\nabla F$,

$$\int \psi_0^{\,2} \, \underset{\sim}{G} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r} = \int \psi_0^{\,2} \left[\underset{\sim}{G} + \nabla F \right] \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r} = 0 \tag{23}$$

Thus, Eq. (19) becomes

$$\epsilon_0^{(2)} = -\tfrac{1}{2} \int \psi_0^{\,2} \, \bar{\underset{\sim}{G}} \cdot \bar{\underset{\sim}{G}} \, d\underset{\sim}{r} + \tfrac{1}{2} \int \psi_0^{\,2} \, \delta \underset{\sim}{G} \cdot \delta \underset{\sim}{G} \, d\underset{\sim}{r} \tag{24}$$

Since the second integral is necessarily positive, the Thomson principle, Eq. (12) is necessarily true.

Comparison of Thomson and Weinstein-MacDonald Principles

The best previous principle for obtaining lower bounds for the energy of the ground state (without requiring knowledge of the energies of excited states) is that of Weinstein and MacDonald[4,5,6]. If H is the Hamiltonian for the system, E_0 is the energy of the ground state, $\bar{\psi}$ is a normalized trial wave function, $J_1 = \int \bar{\psi} \, H \, \bar{\psi} \, d\underset{\sim}{r}$, and $J_2 = \int \bar{\psi} \, H^2 \, \bar{\psi} \, d\underset{\sim}{r}$, then the Weinstein-MacDonald principle states that

$$E_0 \geq J_1 - (J_2 - J_1^{\,2})^{\tfrac{1}{2}} \tag{25}$$

Let us apply this principle to a perturbation problem where $H = h_o + \lambda V$, the energy of the ground state is $E_o = \epsilon_o + \lambda \epsilon_o^{(1)} + \lambda^2 \epsilon_o^{(2)} + \cdots$ and its true wave function is $\psi_o + \lambda F \psi_o + \cdots$. If we suppose that the un-normalized trial wave function is $\psi_o + \lambda \bar{F} \psi_o$, then the Weinstein-MacDonald principle states that

$$E_o \geq \epsilon_o + \lambda \epsilon_o^{(1)} - \lambda \left[\int \left\{ (h_o - \epsilon_o) \bar{F} \psi_o + (V - \epsilon_o^{(1)}) \psi_o \right\}^2 d\underset{\sim}{r} \right]^{\frac{1}{2}}$$

$$+ \lambda^{3/2} (\cdots) + \cdots \tag{26}$$

Since the integrand in Eq. (26) is only zero if $\bar{F}$ is equal to the true function F , the coefficient of the first power of the perturbation parameter on the right-hand-side is not $\lambda \epsilon_o^{(1)}$. Thus, the Weinstein-MacDonald principle does not even accurately predict the first order energy and gives us no information regarding the second-order perturbation energy in this application. Thus, the Thomson principle is unchallenged as our best means for determining the lower bound to the second order perturbation energy.

IV. <u>Upper Bound for $\epsilon_o^{(2)}$, Dirichlet's Principle (Derived from Rayleigh-Ritz Principle)</u>

Dirichlet's principle can be applied to perturbation theory with the same provisos as given for the Thomson principle in Section III. By analogy with Eq. (11),

$$\epsilon_o^{(2)} \leq -2 \left[\int \psi_o (V - \epsilon_o^{(1)}) \psi_o \, \bar{F} \, d\underset{\sim}{r} \right]^2 \bigg/ \int \psi_o^2 \, \nabla \bar{F} \cdot \nabla \bar{F} \, d\underset{\sim}{r} \tag{27}$$

where $\bar{F}$ is any trial function subject to the conditions that it not have any singularities and that $\psi_o^2 \bar{F} \nabla \bar{F}$ approaches zero faster than the square of the distance in the limit as the distance approaches infinity. The equality holds if, and only if, $\bar{F}$ is proportional to the true function F . Furthermore, if $a \bar{F}$ is a trial function, the optimum value of the constant a is

$$a = -2 \int \psi_o (V - \epsilon_o^{(1)}) \psi_o \, \bar{F} \, d\underset{\sim}{r} \Bigg/ \int \psi_o^2 \, \nabla \bar{F} \cdot \nabla \bar{F} \, d\underset{\sim}{r} \qquad (28)$$

Dirichlet's principle is only applicable to molecules in their ground state or the lowest energy state of a given symmetry. Sinanoglu's principle, discussed in Section VI, provides an upper bound for the second order perturbation energy of excited state molecules.

PROOF:

Although the Dirichlet principle can be justified directly by using the standard methods of variational calculus, we shall derive it in two steps starting with the Rayleigh-Ritz minimum energy principle. Using the notation of the previous section, the Rayleigh-Ritz principle states that $E_o \leq J_1$. In a perturbation problem with $H = h_o + \lambda V$, if we evaluate J_1 using the un-normalized trial wave function $\psi_o + \lambda \bar{F} \psi_o$, then the Rayleigh-Ritz principle gives

$$E_o \leq \epsilon_o + \lambda \epsilon_o^{(1)} + \lambda^2 Q + \lambda^3 (\cdots) + \cdots \qquad (29)$$

where

$$Q = \int \bar{F} \psi_o (h_o - \epsilon_o) \psi_o \bar{F} \, d\underset{\sim}{r} + 2 \int \psi_o (V - \epsilon_o^{(1)}) \psi_o \bar{F} \, d\underset{\sim}{r} \qquad (30)$$

Since $E_o = \epsilon_o + \lambda \epsilon_o^{(1)} + \lambda^2 \epsilon_o^{(2)} + \cdots$, we can subtract $\epsilon_o + \lambda \epsilon_o^{(1)}$ from both sides of (29) and divide by λ^2 to obtain

$$\epsilon_o^{(2)} + \lambda \epsilon_o^{(3)} + \cdots \leq Q + \lambda (\cdots) + \cdots \qquad (31)$$

Since Eq. (30) is true for all sufficiently small values of λ, it follows that

$$\epsilon_o^{(2)} \leq Q \qquad (32)$$

This is the Hylleraas principle[4,5,6]. The equality holds if, and only if, the trial function $\bar{F}$ is equal to the true function F . The Hylleraas principle has been used extensively in perturbation theory

to provide a perturbation-variational upper bound on the second order perturbation energy. The Dirichlet principle, Eq. (27), is readily derived from the Hylleraas principle. However, the Dirichlet principle usually gives a closer limit.

The first step in deriving the Dirichlet principle is to examine the first integral in Q. Since $h_o = -\frac{1}{2}\nabla + v_o$ where v_o is the potential energy of the unperturbed system,

$$h_o(\psi_o \bar{F}) = \bar{F} h_o \psi_o - \nabla \psi_o \cdot \nabla \bar{F} - \frac{1}{2}\psi_o \nabla \bar{F} \qquad (33)$$

And, of course, $h_o \psi = \epsilon_o \psi_o$. Thus,

$$\int \bar{F} \psi_o (h_o - \epsilon_o)\psi_o \bar{F} \, dr = -\int \bar{F} \psi_o \nabla \psi_o \cdot \nabla \bar{F} \, dr - \frac{1}{2}\int \bar{F} \psi_o^2 \nabla \bar{F} \, dr$$

$$= -\frac{1}{2}\int \bar{F} \nabla \cdot (\psi_o^2 \nabla \bar{F}) dr \qquad (34)$$

$$= +\frac{1}{2}\int \psi_o^2 \nabla \bar{F} \cdot \nabla \bar{F} \, dr$$

The last step in Eq. (34) is obtained through integration by parts and is only permissible if $\bar{F}$ has no singularities, and $\psi_o^2 \bar{F} \nabla \bar{F}$ approaches zero faster than the square of the distance in the limit as the distance approaches infinity. Thus, the Hylleraas principle can be restated in the form

$$\epsilon_o^{(2)} \leq \frac{1}{2}\int \psi_o^2 \nabla \bar{F} \cdot \nabla \bar{F} \, dr + 2\int \psi_o(V - \epsilon_o^{(1)})\psi_o \bar{F} \, dr \qquad (35)$$

Now, in place of $\bar{F}$, let us use as trial function $a\bar{F}$. Then (35) becomes

$$\epsilon_o^{(2)} \leq \frac{a^2}{2}\int \psi_o^2 \nabla \bar{F} \cdot \nabla \bar{F} \, dr + 2a\int \psi_o(V - \epsilon_o^{(1)})\psi_o \bar{F} \, dr \qquad (36)$$

By varying the constant "a", the right-hand-side of (36) can be minimized and the upper bound for $\epsilon_o^{(2)}$ improved. The optimum value of "a" is given by Eq. (28). Inserting Eq. (28) into (36) gives the Dirichlet principle as expressed in (27).

V. Illustration: Polarizability of 1s Atomic Hydrogen

The polarizability of a hydrogen atom in its ground state provides a good example to illustrate the application of the Thomson and Dirichlet principles. Consider the atom perturbed by a uniform electric field in the x direction. The electric field strength is taken to be the perturbation parameter and $V = -x$. The first-order perturbation energy (or Stark effect) is zero for this case. The polarizability is defined to be $\alpha = -2\epsilon_0^{(2)}$. The 1s wave function for the unperturbed hydrogen atom is $\psi_0 = (\pi)^{-\frac{1}{2}} \exp(-r)$.

Thomson's Principle

Condition (13) becomes for this example,

$$\nabla \cdot \left[\bar{\underset{\sim}{G}} \exp(-2r) \right] = 2 \, x \, \exp(-2r) \tag{37}$$

A possible trial field which satisfies Eq. (37) is

$$\bar{\underset{\sim}{G}} = - (\tfrac{1}{2} + r) \underset{\sim}{j}_x \tag{38}$$

Here $\underset{\sim}{j}_x$ is the unit vector in the x direction. That the trial $\bar{\underset{\sim}{G}}$ of Eq. (38) is not the correct field is evident from the fact that the curl of Eq. (38) does not vanish. Thus, $\bar{\underset{\sim}{G}}$ is not equal to $-\nabla F$. Substituting (38) into (12) gives

$$\epsilon_0^{(2)} > -2.375 \qquad \text{or} \qquad \alpha < 4.75 \tag{39}$$

Dirichlet's Principle

$\bar{F} = ax$ provides a reasonable trial function for use in Dirichlet's principle, (27). The upper bound for $\epsilon_0^{(2)}$ is then

$$\epsilon_0^{(2)} < -2 \left[\frac{1}{\pi} \int x^2 \exp(-2r) d\underset{\sim}{r} \right]^2 = -2 \tag{40}$$

Or, $\alpha > 4$.
According to Eq. (28),

$$a = 2(\pi)^{-1} \int x^2 \exp(-2r) d\underset{\sim}{r} = 2 \qquad (41)$$

Thus, $4.00 < \alpha < 4.75$. The correct value of α is 4.50. By using more complicated functions for $\bar{G}$ and $\bar{F}$, the limits on α can be made as close as desired.

VI. Upper Bound for Excited State $\epsilon_o^{(2)}$, Sinanoglu's Principle

For excited molecular states, the upper bound for $\epsilon_o^{(2)}$ may be obtained from a modification of Sinanoglu's principle[7]:

$$\epsilon_o^{(2)} \leq - \left[\int \psi_o (V - \epsilon_o^{(1)}) \bar{F} \psi_o \, d\underset{\sim}{r} \right]^2 \Big/ \int \bar{F} \psi_o (h_o - \epsilon_o) \bar{F} \psi_o \, d\underset{\sim}{r} \qquad (42)$$

subject to the condition that

$$\int \psi_s \bar{F} \psi_o \, d\underset{\sim}{r} = (\epsilon_o - \epsilon_s)^{-1} \int \psi_s V \psi_o \, d\underset{\sim}{r} \qquad (43)$$

for all states "s" which are lower in energy than the "o" state under consideration, $\epsilon_o > \epsilon_s$. The trial function $\bar{F}$ is further restricted by the requirement that $\bar{F} \psi_o$ satisfy the same boundary, continuity, and integrability conditions required of ψ_o. The equality in (42) holds if, and only if, $\bar{F}$ is proportional to the true F. Furthermore, if $a \bar{F}$ is a trial function, the optimum constant a is

$$a = - \int \psi_o (V - \epsilon_o^{(1)}) \bar{F} \psi_o \, d\underset{\sim}{r} \Big/ \int \bar{F} \psi_o (h_o - \epsilon_o) \bar{F} \psi_o \, d\underset{\sim}{r} \qquad (44)$$

PROOF:

The proof of the modified Sinanoglu principle is very similar to the proof of the Dirichlet principle given in Section IV. We use for the un-normalized trial wave function $\psi_o + \lambda F \psi_o$. Because of the conditions given by Eq. (43), this trial wave function is orthogonal to all of the lower energy states of the system. Because of this orthogonality[4] $E_o \leq J_1$. Thus, with the conditions of Eq. (43), the Hylleraas principle, Eq. (32), still applies. The principle which

Sinanoglu derived[7] is a combination of Eq. (32) with the conditions of Eq. (43).

For excited states, the Hylleraas principle cannot be rearranged into the form of Eq. (35) since $\bar{F}$ may have poles at places where ψ_o has nodes and therefore Gauss' theorem may not be used in Eq. (34). By using as trial function a $\bar{F}$, the Hylleraas principle (32) becomes

$$\epsilon_o^{(2)} \le a^2 \int \bar{F}\, \psi_o (h_o - \epsilon_o)\bar{F}\, \psi_o \; d\underset{\sim}{r} + 2a \int \psi_o (V - \epsilon_o^{(1)})\bar{F}\, \psi_o \; d\underset{\sim}{r} \qquad (45)$$

By varying the constant "a", the right-hand-side of (45) can be minimized and the upper bound for $\epsilon_o^{(2)}$ improved. The optimum value of "a" is given by Eq. (44). Inserting Eq. (44) into (45) gives the modified Sinanoglu principle as expressed in (42).

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